



Designation: D 5174 – 9702

Standard Test Method for Trace Uranium in Water by Pulsed-Laser Phosphorimetry¹

This standard is issued under the fixed designation D 5174; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of total uranium, by ~~mass~~, concentration, in water in the range of 0.05 ppb or greater. Samples with uranium by mass, levels above the laser phosphorimeter dynamic range may be diluted to bring the concentration to a measurable level.

1.2 This test method was used successfully with reagent water. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

1.3 The values stated in SI units are to be regarded as the standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

¹ This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.04 on Methods of Radiochemical Analysis.

Current edition approved ~~Aug. Feb. 10, 1998; 2002~~. Published ~~February 1998; May 2002~~. Originally published as D 5174 – 91. Last previous edition D 5174 – 94~~7~~.

D 1129 Terminology Relating to Water²

D 1193 Specification for Reagent Water²

D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water²

D 3370 Practice for Sampling Water from Closed Conduits²

D 3856 Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water²

D 5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis³

E 131 Terminology Relating to Molecular Spectrometry^{3,5}

3. Terminology

3.1 Definitions:

3.1.1 For definitions of terms used in this test method, refer to Terminologies D 1129 and E 131.

3.1.2 For terms not defined in this test method or in Terminology D 1129 or E 131, reference may be made to other published glossaries.⁶

4. Summary of Test Method

4.1 This test method is based on the utilization of a laser phosphorimeter to determine total uranium, by mass, in water samples.

4.2 A sample aliquot is pipetted into a pretreated glass vial. Concentrated HNO₃ and hydrogen peroxide are added and the sample heated to near dryness. This step is repeated as necessary and the residue is dissolved in dilute HNO₃. A complexant is added to an aliquot of this sample and analyzed in the phosphorimeter.

4.3 For screening purposes only, an aliquot of the sample may be pipetted directly into the phosphorimeter cell and read. This cannot be done if the sample was preserved with HCl or if the matrix is not known.

5. Significance and Use

5.1 This test method is useful for the analysis of total uranium in water following wet-ashing, as required, due to impurities or suspended materials in the water.

6. Interferences

6.1 *Absorption (Inner Filter Effect)*—This effect is more severe with ultraviolet excitation light (337 nm) than with visible excitation because many prevalent compounds have pi-bonding and absorb strongly in this region. Ferric iron and oxy-anions such as nitrate and organic acids are examples. Visible excitation (425 nm) may be absorbed by yellow solutions, for example, chromate. The consequences of this may be reduced signals and low analysis results.

6.2 *Lumiphors*—Many organic substances, such as humic acids and organic degradation products from incomplete ashing emit luminescence of varying lifetimes after excitation. An advantage of phosphorescence measurement is the ability to determine if interferences are present by observing the lifetime of the decay.

6.3 *Quenching*—Shortened triplet-state lifetime and reduced phosphorescence intensities of the excited uranyl complex result when quenching occurs. Reliable results cannot be obtained when quenching exceeds 80 to 90 %. Reducing agents such as alcohols, halides except fluoride, and metals with electronic energy levels overlapping those of uranyl ion are strong quenching agents. Examples are silver, lead, iron (II), manganese (II), and thallium. Results from single time-gated instruments are particularly sensitive to even mild quenching agents such as aluminum (III), magnesium (II), calcium (II), and strontium (II).

6.4 *Competing Reactions*—For this test method to perform well, the uranyl ion must be protected from various intermolecular mechanisms which rapidly quench the uranyl luminescence. Complexation fulfills this need, and examples of effective agents are phosphoric acid, and polyphosphates (Fluran, and Uraplex⁷ and Uraplex⁸).

6.5 Hydrochloric acid, if present, is an interference unless eliminated during digestion.

6.6 If the concentration of uranium in the samples is high enough so that they can be diluted 1/100 with the appropriate nitric acid matrix, then interferences are reduced by diluting their effect.

7. Apparatus

7.1 *Laser Phosphorimeter*,⁹ meeting the following criteria:

7.1.1 *Detection Limit*—The detectable level for uranium must be 0.05 ng/mL or less.

7.1.2 *Dynamic Range*—The phosphorimeter must handle an analytical range of 400 or greater.

7.1.3 *Instrumental Precision*—The precision of repetitive measurements must be within 15 % relative standard deviation (R.S.D.).

7.2 *Labware*—If samples containing less than 0.1 ppb uranium are to be analyzed, digestion vessels (both TFE-fluorocarbon and glassware) if used, and liquid scintillation vials should be leached in hot 4 M nitric acid ~~(1+3)~~ and rinsed thoroughly with deionized water before using. This is necessary to reduce sample contamination from leachable uranium.

² Annual Book of ASTM Standards, Vol 11.01.

³ Annual Book of ASTM Standards, Vol-03.06: 11.02.

8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society.¹⁰⁻¹⁰ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagent blanks shall be run with all determinations.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193, Type ~~HH-I~~ I or better.

8.3 *Hydrogen Peroxide*—Standard 30 % solution of hydrogen peroxide (H₂O₂); commercially available reagent grade.

8.4 *Nitric Acid*—(sp gr 1.42) concentrated nitric acid (HNO₃).

8.5 *Nitric Acid 4 M(1 + 3)*—Add one volume of concentrated nitric acid (HNO₃) to 3 volumes of reagent water, Type ~~I~~. ~~This solution is 4 μ-1~~ I or better.

NOTE 1—Reagent blank shall be run on the concentrated nitric acid to analyze for the level of uranium.

8.6 *Uranium Complexant*—Phosphoric acid, Fluran,⁶ or Uraplex⁷ are some complexants that may be used.

9. Calibration and Standardization

9.1 *Preparation of Standards and Sample for Laser Measurement*—Standards and samples shall be prepared in a similar matrix for phosphorimetric measurement. The final sample preparation step puts uranium into a ~~1+19~~ 0.8 M HNO₃ matrix. Use uranium standards traceable to a National Standardizing Laboratory such as NIST or NPL.

9.2 *Calibration of Phosphorimeter*—The instructions for the operation of the laser phosphorimeter are provided by the manufacturer. The phosphorimeter should be calibrated daily and the calibration verified with standards obtained from a different stock solution than used to prepare the calibration standards.

10. Sampling

10.1 Collect the sample in accordance with the applicable methods as described in Practice D 3370.

11. Procedure

101.1 Pipet 5.0 mL of sample into a glass vial previously treated as described in 7.2.

101.2 Add 1 mL of concentrated HNO₃ and two ~~to~~ or three drops of 30 % hydrogen peroxide.

101.3 Place the vial on a hot plate and heat to dryness. Take care that spattering of the sample does not occur.

NOTE 2—Placing the vial in a 50-mL beaker makes it easier to handle and not so apt to be knocked over.

101.4 Remove the vials from the hot plate and add 1 mL of concentrated HNO₃, two ~~to~~ or three drops of 30 % hydrogen peroxide, and heat to dryness. Repeat as necessary until only a white or translucent residue remains.

101.5 Add 1.0 mL of 4 M HNO₃(~~1+3~~) and warm gently, if necessary, to dissolve the residue. Then add 4.0 mL of water conforming to Specification D 1193, Type I or better. Swirl to mix thoroughly.

101.6 Analyze the solution according to the instruction manual provided with the phosphorimeter.

NOTE 3—If the concentration of uranium in the prepared sample is high such that it is out of range of the calibrations, dilutions should be made using HNO₃(~~1+19~~); 0.8 M, which is the concentration of nitric acid in the final sample preparation.

11. Calculation

11.1 Refer to the instrument manual for explanation of calculations.

⁵ See *American National Standard Glossary*

⁵ *Annual Book of Terms in Nuclear Science and Technology* (ANSI N1.1), available from American National ASTM Standards Institute, 1430 Broadway, New York, NY 10014., Vol 03.06.

⁶ ~~See~~ *American National Standard Glossary of Terms in Nuclear Science and Technology* (ANSI N1.1), available from ~~Scintrex, DMW Geophysical Services, 2558 E. Montebellow, Sandy, UT 84092, has been found satisfactory for this purpose.~~ American National Standards Institute, 1430 Broadway, New York, NY 10014.

⁷ Uraplex;

⁷ Fluran, available from ~~Chemchek Instruments, Inc., 1845 Terminal Drive, Richland, WA 99352;~~ Scintrex, DMW Geophysical Services, 2558 E. Montebellow, Sandy, UT 84092, has been found suitable satisfactory for this purpose.

⁸ Instruments;

⁸ Uraplex, available from ~~Chemchek Instruments, Inc., 1845 Terminal d Drive, Richland, WA 99352, and~~ Scintrex, DMW Geophysical Services, 2558 E. Montebellow, Sandy, UT 84092, have has been found suitable for this purpose. ~~Consult appropriate equipment manuals for explanations of calibration and calculations.~~

Reagent Chemicals, American Chemical Society Specifications. American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Anular Standards*

⁹ Instruments, available from ~~Chemchek Instruments, Inc., 1845 Terminal drive, Richland, WA 99352, and~~ Scintrex, DMW Geophysical Services, 2558 E. Montebellow, Sandy, UT 84092, have been found suitable for ~~Laboratory Chemicals, BDH Ltd., Poole, Dorset, U.K.; this purpose. Consult appropriate equipment manuals for explanations of calibration and the United States Pharmacopeia and National Formulatory, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD, calculations.~~

¹⁰ Supporting data available from ASTM Headquarters. Request RR:D-19-1148.

¹⁰ *Reagent Chemicals, American Chemical Society Specifications.* American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Anular Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the United States Pharmacopeia and National Formulatory, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

11.2 Estimate the uncertainty of analysis by performing replicate analyses at different known concentrations and calculating the bias and standard deviation as a function of concentration.

11.3 Estimate the minimum detectable concentration by multiplying the standard deviation of replicate reagent blank analyses by 4.65.

12. Calculation

12.1 Refer to the instrument manual for explanation of calculations.

12.2 Estimate the uncertainty of analysis by performing replicate analyses at different known concentrations and calculating the bias and standard deviation as a function of concentration.

12.3 Estimate the minimum detectable concentration (MDC) by multiplying the standard deviation of replicate reagent blank analyses by 4.65 and adjusting for the recovery as shown below. Equation for calculating the *a priori* minimum detectable concentration (MDC):

$$MDC = 4.65 * \frac{S_b}{R} \quad (1)$$

where:

MDC = the minimum detectable concentration,

4.65 = Currie constant,

S_b = standard deviation of the blank in concentration, and

R = chemical recovery (average or batch).

13. Precision and Bias ¹¹

123.1 The collaborative test conducted on this test method included six laboratories for Level 1 and seven laboratories for Levels 2 and 3. There were a total of three levels between 1 and 100 µg/L with three replicates per level. The determination of the precision and bias statements were made in accordance with Practice D 2777.

123.2 These collaborative test data were obtained using reagent grade water. For other matrices, these data may not apply.

123.3 The bias of this test method, based upon the collaborative test data, was found to vary with level according to Table 1.

123.4 The overall and single operator precision have been found to vary with level according to Table 2.

13. Quality Control

13.1 Whenever possible, the project leader, as part of the external quality control program, should submit quality control samples to the analyst along with routine samples in such a way that the analyst does not know which of the samples are the quality control samples. These external quality control samples which usually include duplicate and blank samples, should test sample collection and preparation as well as sample analysis whenever this is possible. In addition, analysts are expected to run internal quality control samples that will indicate to them whether the analytical procedures are in control. Both the external and internal quality control samples should be prepared in such a way as to duplicate the chemical matrix of the routine samples, insofar as this is practical. The quality control samples that are routinely used consist of five basic types: blank samples, replicate samples, reference materials, control samples, and spiked samples.

14. Quality Control

14.1 In order to be certain that analytical values obtained using this test method are valid and accurate within the confidence limits of the test the following QC procedures must be followed when running the test. The batch size should not exceed 20 samples, not including QC samples.

14.2 *Calibration and Calibration Verification:*

14.2.1 Using three standards of different concentrations, prepare a calibration curve for both the low and high measurement ranges. Typically the low and high ranges are 0.5 to 10 ng/mL and 10 to 300 ng/mL respectively. The calibration is performed each day of use.

14.2.2 A verification standard prepared at a concentration within the calibration range is analyzed immediately following the calibration and at least once per shift thereafter.

¹¹ Supporting data available from ASTM Headquarters. Request RR:D-19-1148.

TABLE 1 Uranium in Water by Phosphorimetry (Digestion Method) Bias Data

| Amount Added, µg/L | Amount Found, µg/L | Bias, % |
|--------------------|--------------------|---------|
| 2.25 | 2.26 | 0.44 |
| 42.30 | 43.18 | 2.08 |
| 84.60 | 89.11 | 5.33 |

TABLE 2 Uranium in Water by Phosphorimetry (Digestion Method) Pooled Single Operator Precision (S_o) and Overall Precision (S_t)

| Amount Added, µg/L | S _o , µg/L | S _t , µg/L |
|--------------------|-----------------------|-----------------------|
| 2.25 | 0.09 | 0.27 |
| 42.30 | 1.41 | 2.48 |
| 84.60 | 1.98 | 5.53 |

14.2.3 Acceptance limits for the verification standard are 90-110%. If the results for the verification standard are outside the limits, recalibrate and reanalyze samples back to the last valid verification standard.

14.3 Initial Demonstration of Instrument Capability:

14.3.1 If a laboratory has not performed this test before or there has been a major change in the measurement system, for example, significant instrument change, new instrument, etc., a precision and bias study must be performed to demonstrate instrument capability.

14.3.2 Analyze seven replicates of a standard solution prepared from an IRM containing accurately known concentrations of approximately 2, 40 or 80 µg/L of uranium.

14.3.3 Calculate the mean and standard deviation of the values obtained from the analysis and compare to the laboratory specified acceptable ranges of precision and bias, to those in the following table or to those specified by the customer. This study should be repeated until the precision and the mean recovery is within the specified limits. If a concentration other than the recommended concentration is used, refer to Test Method D 5847 for information on applying the F test and t test in evaluating the acceptability of the mean and standard deviation.

| Amount Added, µg/L | Precision (S _o), % | Bias (S _b), % |
|--------------------|--------------------------------|---------------------------|
| 2.25 ^A | 4.0 | 12.0 |
| 42.3 ^A | 3.3 | 5.9 |
| 84.6 ^A | 2.3 | 6.5 |

^AThe collaborative test conducted on this test method included six laboratories for Level 1 and seven laboratories for Levels 2 and 3.

14.3.4 If this demonstration is performed to confirm instrument performance, verify that the MDC has not changed.

14.4 Demonstration of Capability:

14.4.1 To demonstrate capability each analyst must analyze a blank and four replicates of a standard solution prepared from an IRM containing accurately known concentrations of approximately 2, 40 or 80 µg/L of uranium or concentrations acceptable to the customer. The matrix and chemistry should be equivalent to the samples to be analyzed. Each replicate and the blank must be taken through the complete analytical test method including any sample preservation and pretreatment steps.

14.4.2 Compare the results of the replicates and the blank to the laboratory or customer control limits. If the results are not within the control limits repeat the analyses.

14.5 Laboratory Control Sample (LCS):

14.5.1 To ensure that the test method is in control, analyze a LCS with each batch of no more than 20 samples. The concentration added to reagent water should be appropriate for the type of samples analyzed and allow sufficient precision to insure a meaningful assessment of accuracy. The LCS must be taken through all the steps of the analytical method including sample preservation and pretreatment. The result obtained for the LCS shall fall within the limit of ± 25 % of the expected value or within a limit that is compliant with the data quality objectives or the applicable regulations.

14.5.2 If the result is not within these limits, reporting of the results is halted until the problem is resolved. An indication of the occurrence should accompany the reported results.

14.6 Method Blank:

14.6.1 Analyze a reagent water test blank with each batch of no more than 20 samples. The concentration of analyte found in the blank should be less than half the MDC. If the concentration of the analyte is found above this level, the results must be flagged.

14.7 Matrix Spike:

14.7.1 Analyze at least one matrix spike sample with each batch of no more than 20 samples by spiking an aliquot of a sample within the batch with a known concentration of uranium and analyze in the same manner as the other samples in the batch.

14.7.2 The spike should produce a concentration of uranium that is 2 to 5 times the anticipated sample concentration or as specified by the laboratory, whichever is greater.

14.7.3 Calculate the recovery (R) of the matrix spike using the following formula:

$$R = (A_{as} - A_a) / A_s \quad (2)$$

Where:

- R ≡ recovery,
- A_{as} ≡ analyte amount plus spike amount in mass units,
- A_a ≡ analyte amount in mass units, and
- A_s ≡ spike amount in mass units.

Alternatively add "C" after each of the symbols above to indicate concentration results.

14.7.4 R should fall within the limit of $\pm 50\%$ of the expected value. If the concentration is not within these limits, provide an explanation in the case narrative.

14.8 Duplicate:

14.8.1 Analyze a sample in duplicate with each batch of no more than 20 samples.

14.8.2 In the absence of laboratory specified control limits, compare to the single operator precision using an F test.

14.8.3 If the result exceeds the precision limit, the results must be flagged.

14.9 Independent Reference Material (IRM):

14.9.1 Analyze an IRM, such as a performance evaluation sample, at least once per quarter. The value should fall within the laboratory specified control limits, if not corrective action may need to be considered.

15. Keywords

145.1 laser; phosphorescence; phosphorimetry; uranium; water

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org).